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REVERSIBLE SOLID OXIDE CELLS: LIMITATIONS AND POSSIBILITIES

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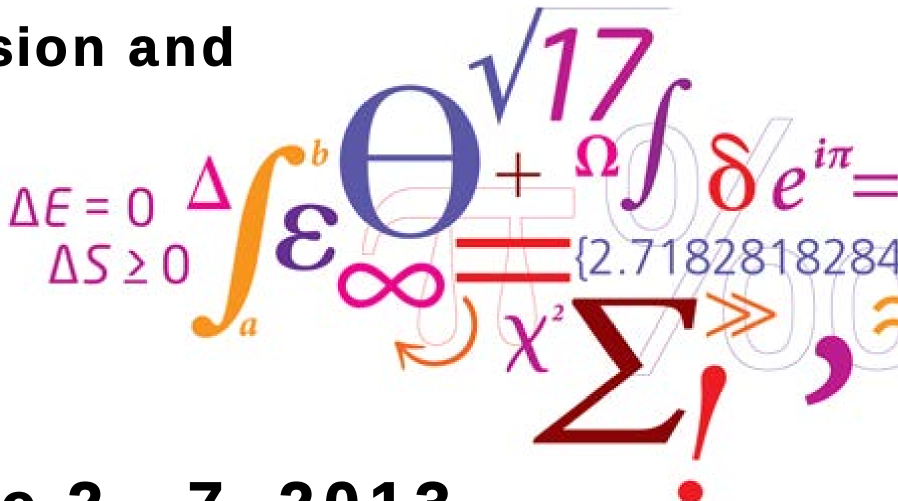


Invited presentation

SSI-19 Kyoto, Japan, June 2 - 7, 2013

Outline

1. Introduction
2. SOC type and performance
3. Thermodynamic stability of materials and gases
4. Temperature gradients and mechanical stability
5. Possibilities - what to do?
6. Conclusions

Introduction

- We need conversion and storage devices to promote renewable energy from intermittent sources such as wind and solar

- Solid oxide cell (SOC) may be used as solid oxide electrolysis cell (SOEC) as well as solid oxide fuel cell (SOFC); it is fully reversible for H_2O/H_2 and CO_2/CO and mixtures of them

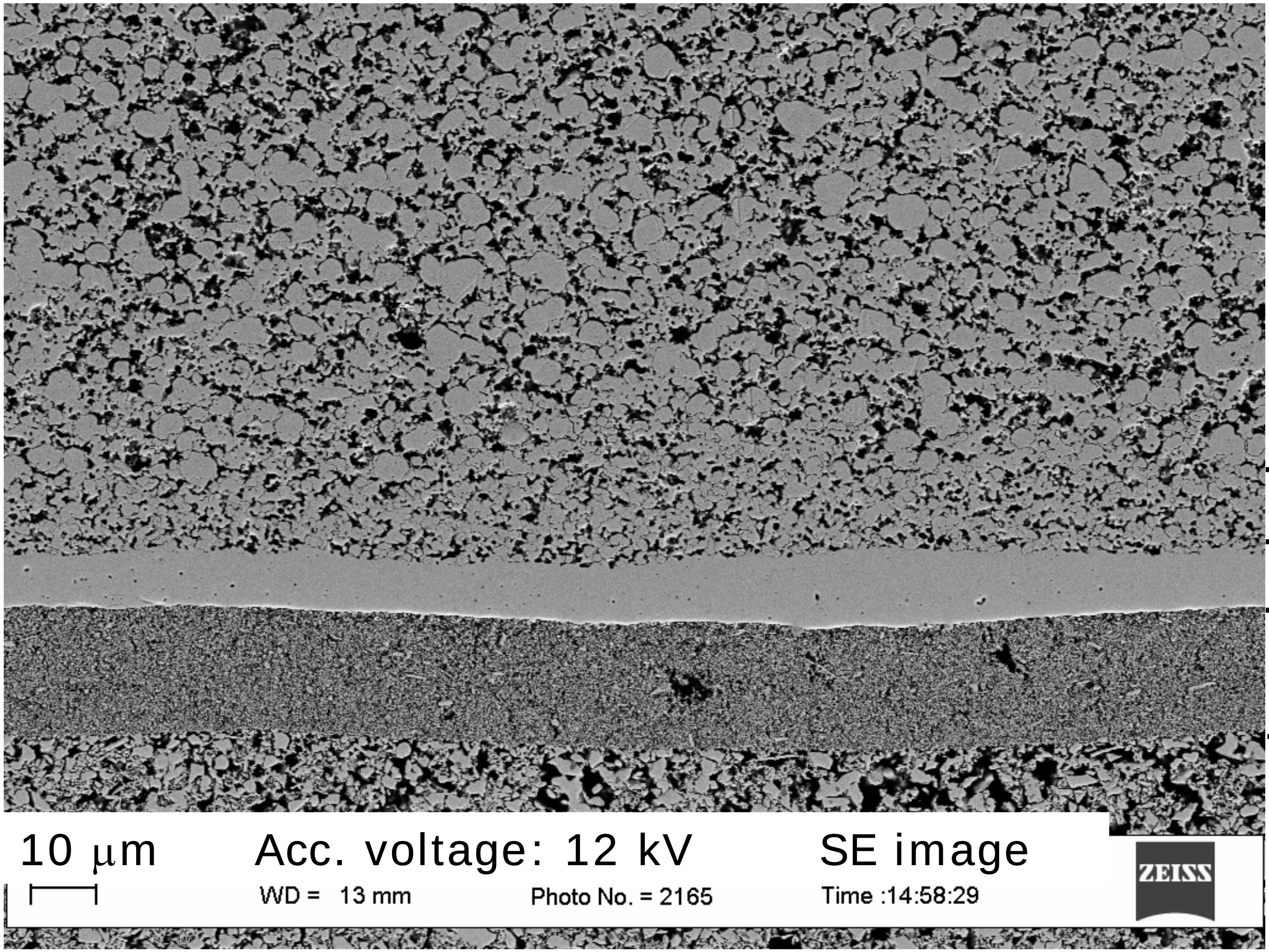
- SOC has a considerable potential in this context, but is not the market yet in spite of several decades of intense R&D

- What are the limitations?

- Are there possibilities to push the limitations?

SOC type

Ni-YSZ supported



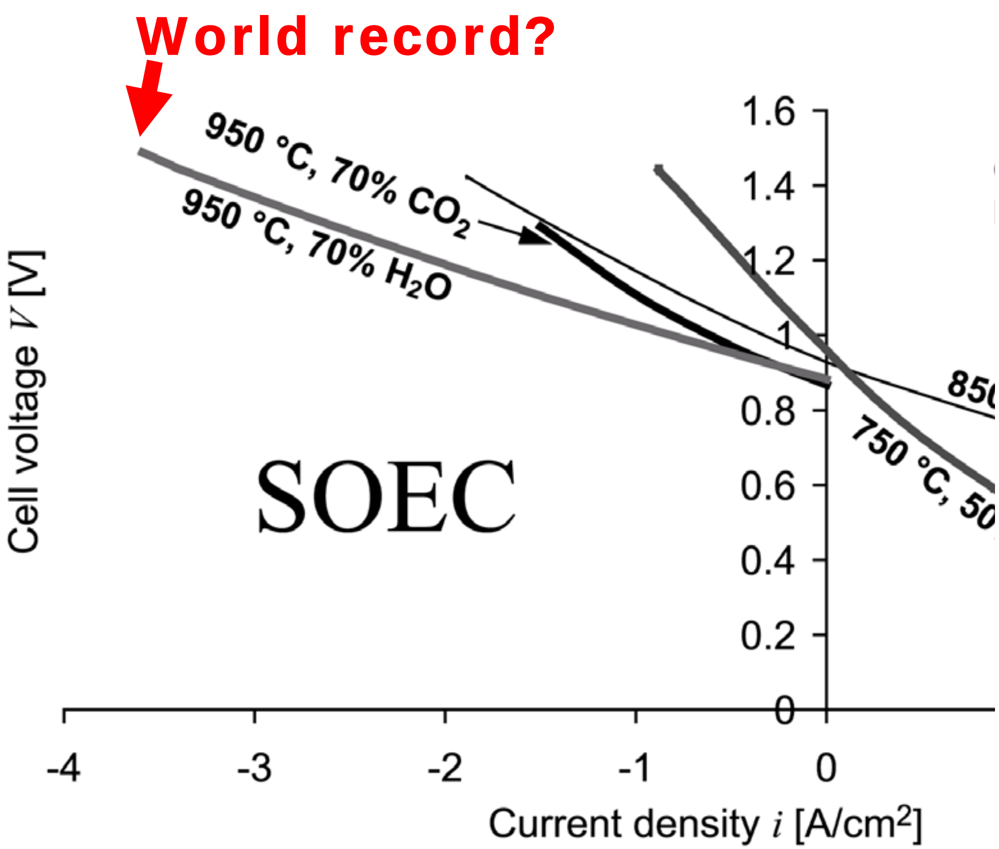
Ni / YSZ support

Ni / YSZ electrode

YSZ electrolyte

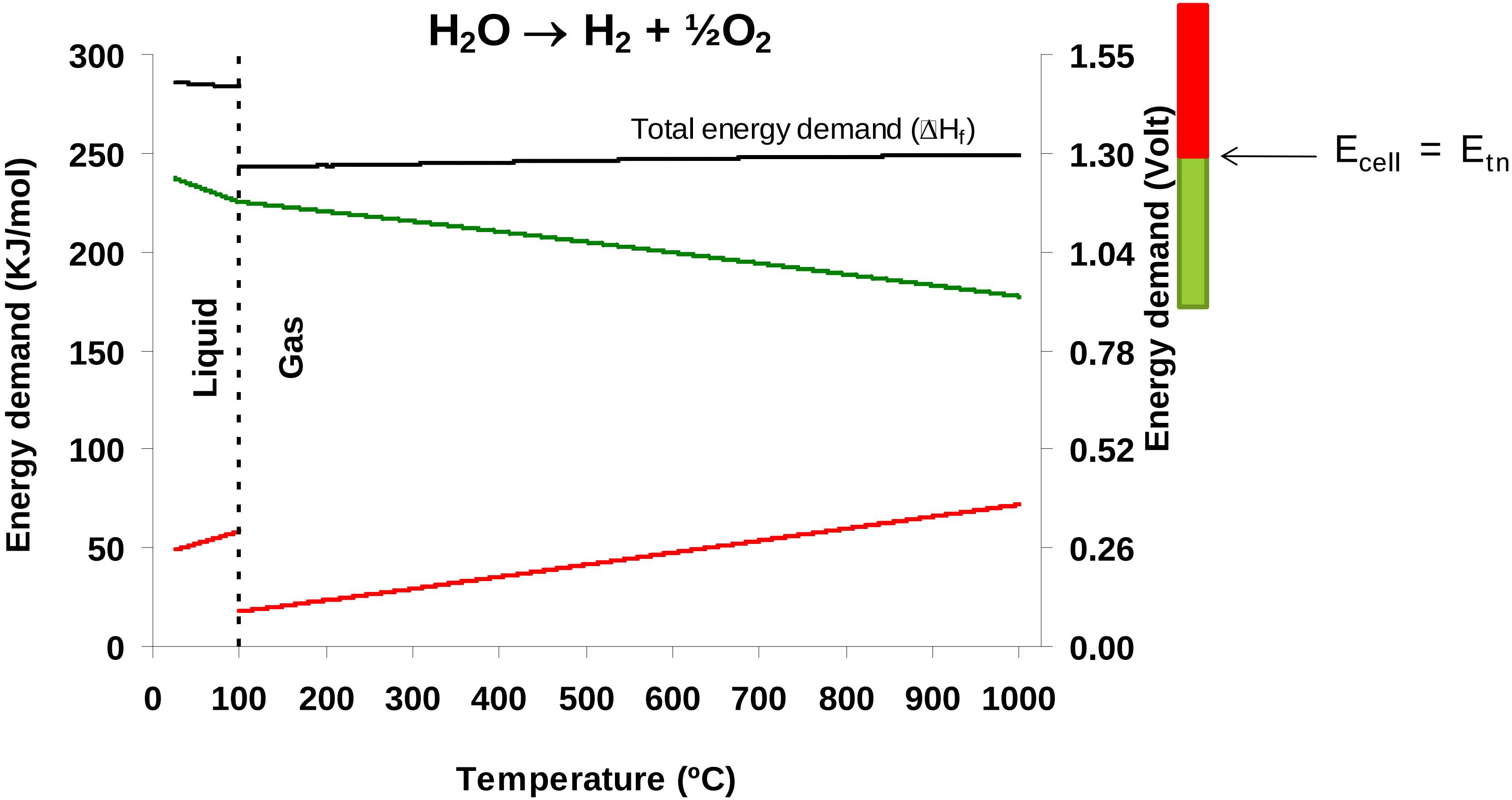
LSM-YSZ electrode

SOEC Cell performance



i - V **curves for a Ni-YSZ-supported Ni / YSZ / LSM SOC: electrolyzer (negative current density) and fuel cell (positive current density) at different temperatures and steam or CO_2 partial pressures - balance is H_2 or CO.** **S.H. Jensen et al., International Journal of Hydrogen Energy, 32 (2007) 3253**

Thermodynamics of H_2Oelectrolysis



Energy ("volt") = Energy (kJ/mol)/2F

$i \propto E_{cell} - \Delta G/2F$

$E_{tn} = \Delta H/2F$

Price $\propto$ 1/i [A/cm^2] ,

$\Delta H/\Delta G > 1$, $\varepsilon = 100\,\%$ at $E = E_{tn}$ (if no heat loss)

Thermodynamic stability of materials and gases

- Often degradation rates are reported as a function of current density even though it most often would be more appropriate to report as a function of electrode potentials and overpotentials.

- Naturally, the overvoltage and current density are directly related for a given of cell, but

- Thermodynamic stability is directly related to electrode potential (vs. a reference, e.g. 1 atm. O_2 at given temperature) for given cell materials irrespective structural details such as particle size in composite electrodes.

Thermodynamic and mechanical stability of YSZ, Ni-YSZ, LSM-YSZ, CO etc.

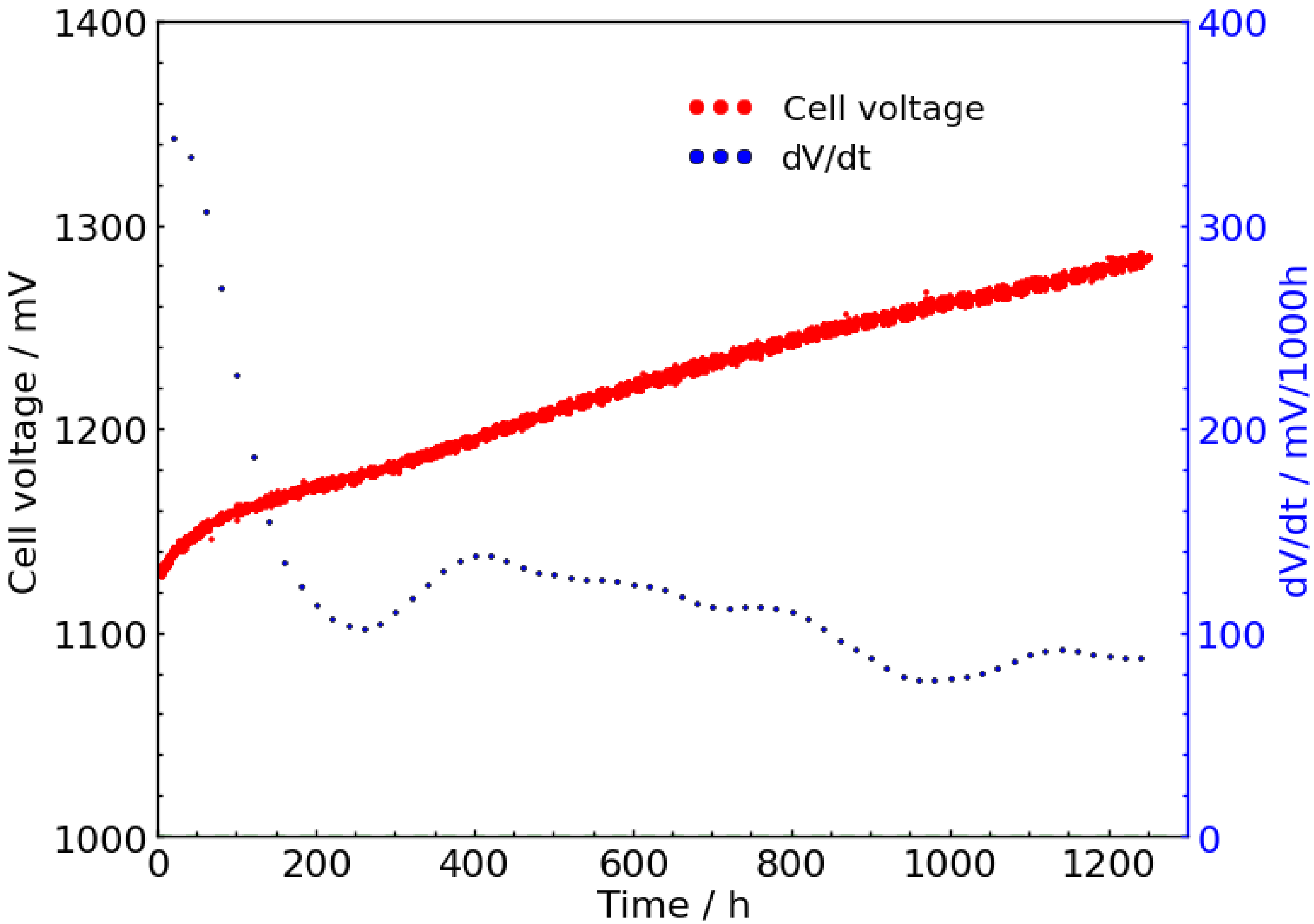
- $\Delta G_f \approx -975$ kJ/mol ZrO_2 at 800 °C ~ a voltage stability range of ca. 2.5 V - the very maximum, but realities are worse

- SOFC mode:
  - reactions between La,Sr based perovskite oxygen electrodes and YSZ
  - Re-oxidation of Ni in Ni-YSZ – the redox problem

- SOEC mode:
  - 1 ppm Zr into Ni at ca. -1.5 V, 850 °C - impurities make worse M. Chen et al., J. Electrochem. Soc., 160 (2013) F883
  - carbon fiber formation in CO_2-H_2O co-electrolysis if high diffusion limitation, Y. Tao et al., submitted to ECST
  - O_2 bubble formation with weakening of YSZ near LSM at high oxygen electrode overpotential (~ 60 mV at 850 °C), R. Knibbe et al., J. Electrochem. Soc., 157 (2010) B1209

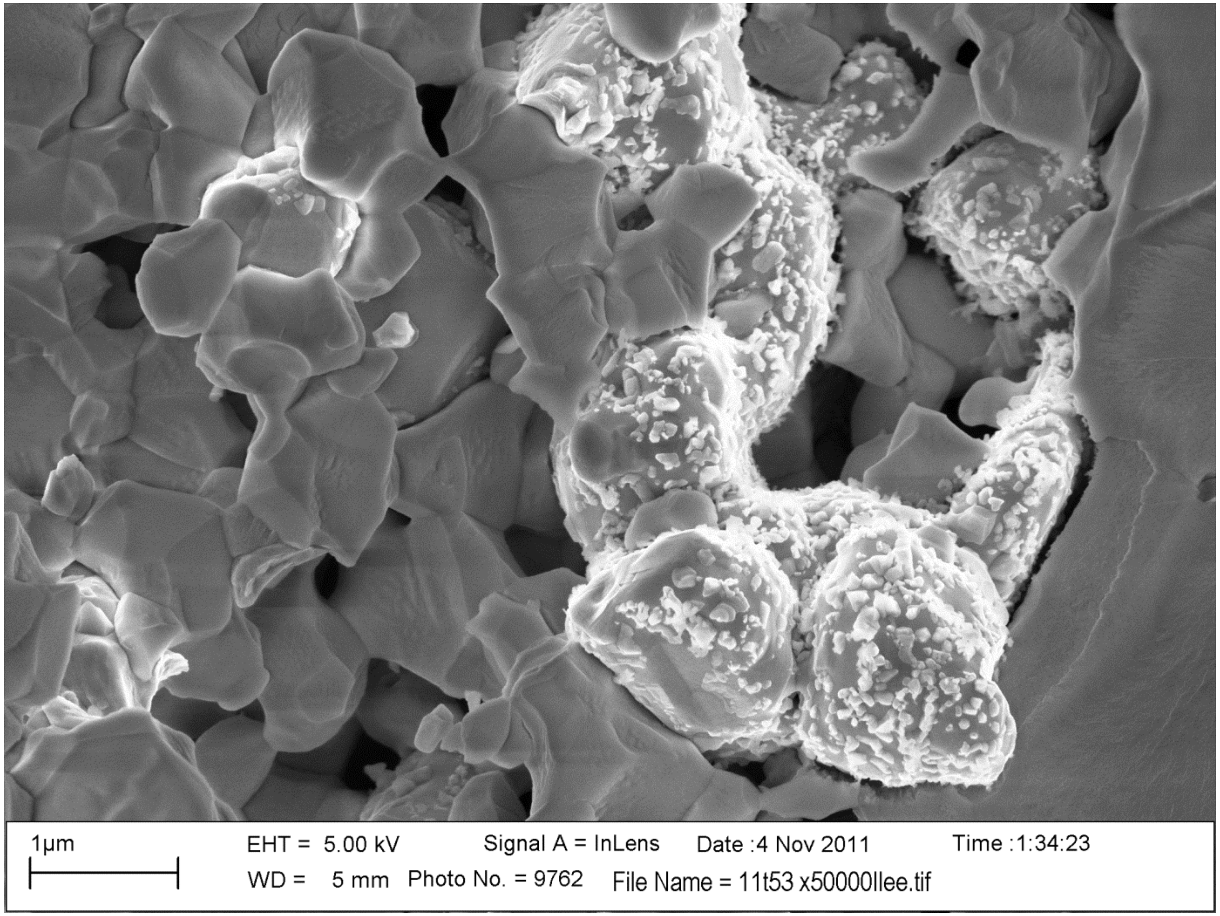
- Mechanical strength: limitation for ceramic supported cells!

SOC degradation – in a bad case



850 °C, 10 % H_2 + 45 % H_2O + 45 % CO_2 to Ni/YSZ electrode and O_2 at LSM/YSZ electrode. Current density -1 A/cm^2, conversion degree 62 %.

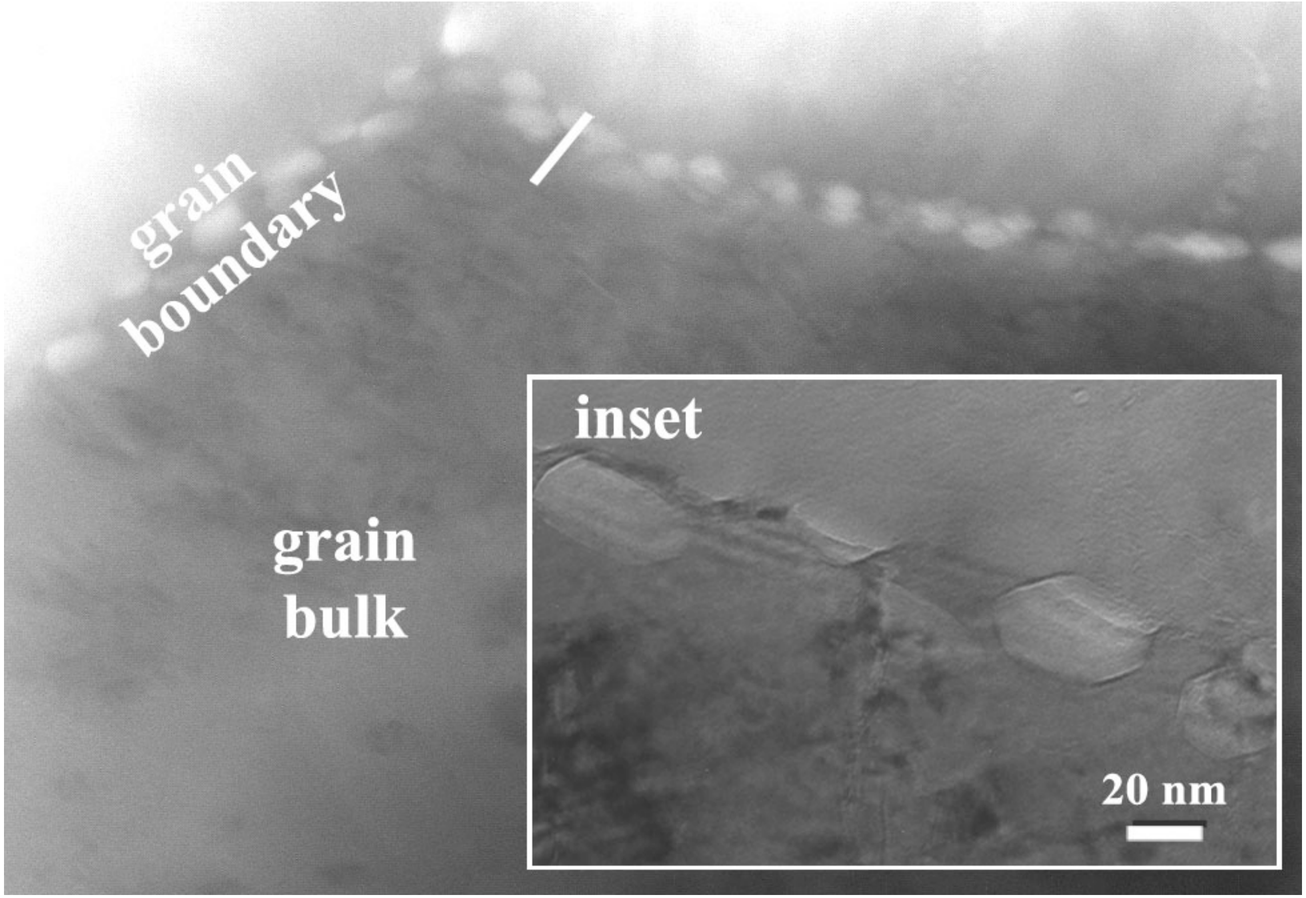
Ni-YSZ cermet after test in previous graph



Detrimental nano-particle formation on Ni-particle surfaces breaking good contact to YSZ

Fast degradation > ca. 1 A cm^{-2}

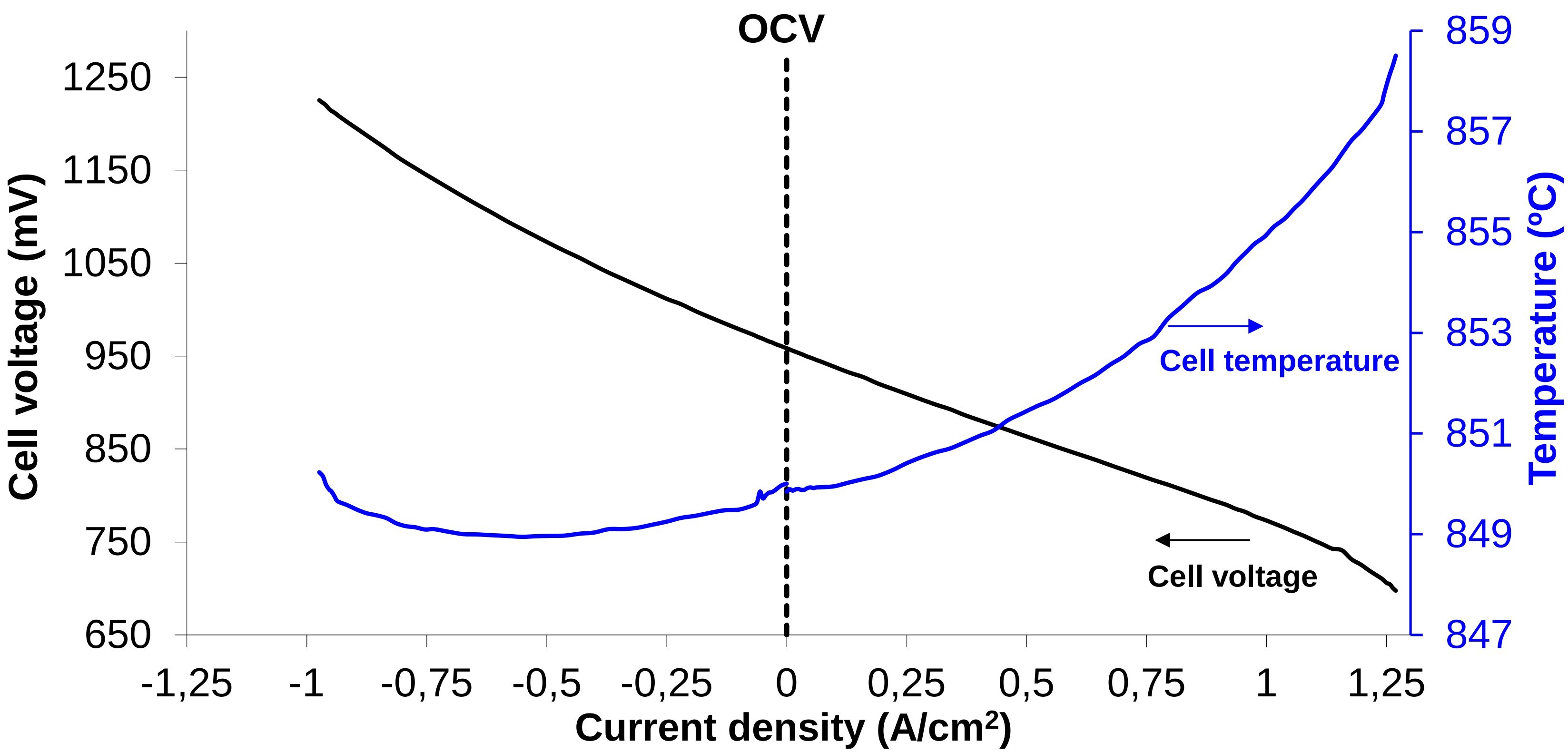
- 850 °C, single cell, steam, -2 A cm^{-2} for 188 h
- Electrolyte conductivity degradation - near oxygen electrode
- TEM reveals that it is due to O_2 bubble precipitation inside the electrolyte near the O_2 LSM / YSZ-electrode destroying $\sigma_{O^{2-}}$



Ruth Knibbe et al., J. Electrochem. Soc., **157** (2010) B1209

This is to an extent a mechanical problem – O_2 bubble formation is limited by YSZ creep only

Thermal aspects – temperature gradients?



Temperature measured outside cell - on O_2-electrode side

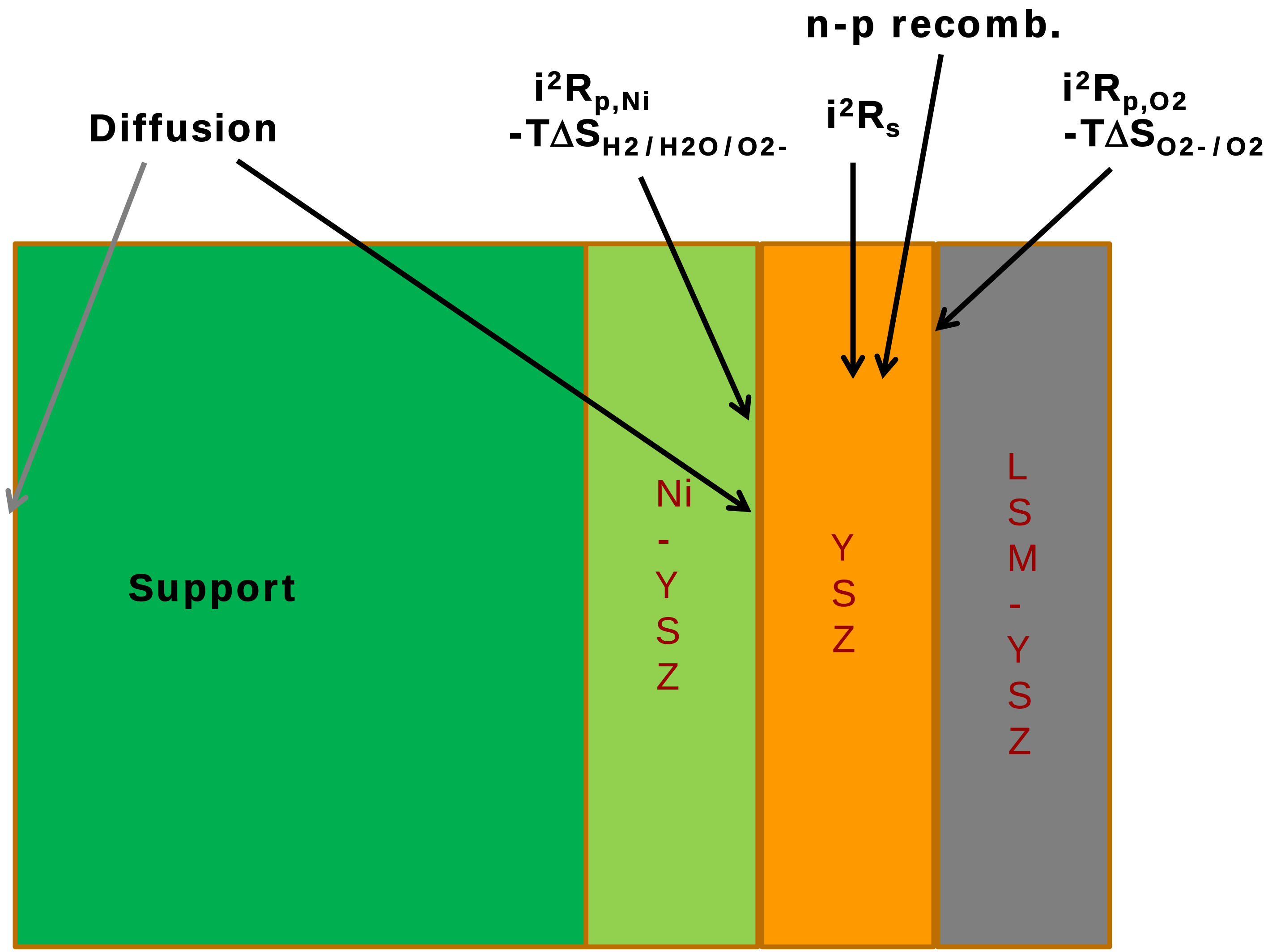
S. Ebbesen et al. Submitted to ECST

In-plane cracks in the YSZ near LSM electrode

is often observes after test at high current density > 1 A cm^{-2}

Could this be due to thermal gradients?

Heat sources



Heat sources

- i^2R_x is always positive heat irrespective og SOFC or SOEC
- Diffusion is always positive heat

- Reversible Peltier entropies of the single electrode reactions have a different nature:
- Oxygen electrode, SOFC cathode: ΔS_c = 46.9 J K^{-1} (mol e^-)$^{-1}$
- Hydrogen electrode, SOFC anode: ΔS_a = -31.8 J K^{-1} (mol e^-)$^{-1}$
- $-T\Delta S_c$ is positive heat in SOFC mode and negative heat (i.e. cooling) in SOEC mode

$2\ O^{2-} \rightarrow O_2 + 4\ e^-$ 850 °C: $T\Delta S_c$ = +50.3 kJ (mol e^-)$^{-1}$

$2\ H_2O + 4\ e^- \rightarrow 2\ H_2 + 2\ O^{2-}$ 850 °C: $T\Delta S_a$ = -34.1 kJ (mol e^-)$^{-1}$

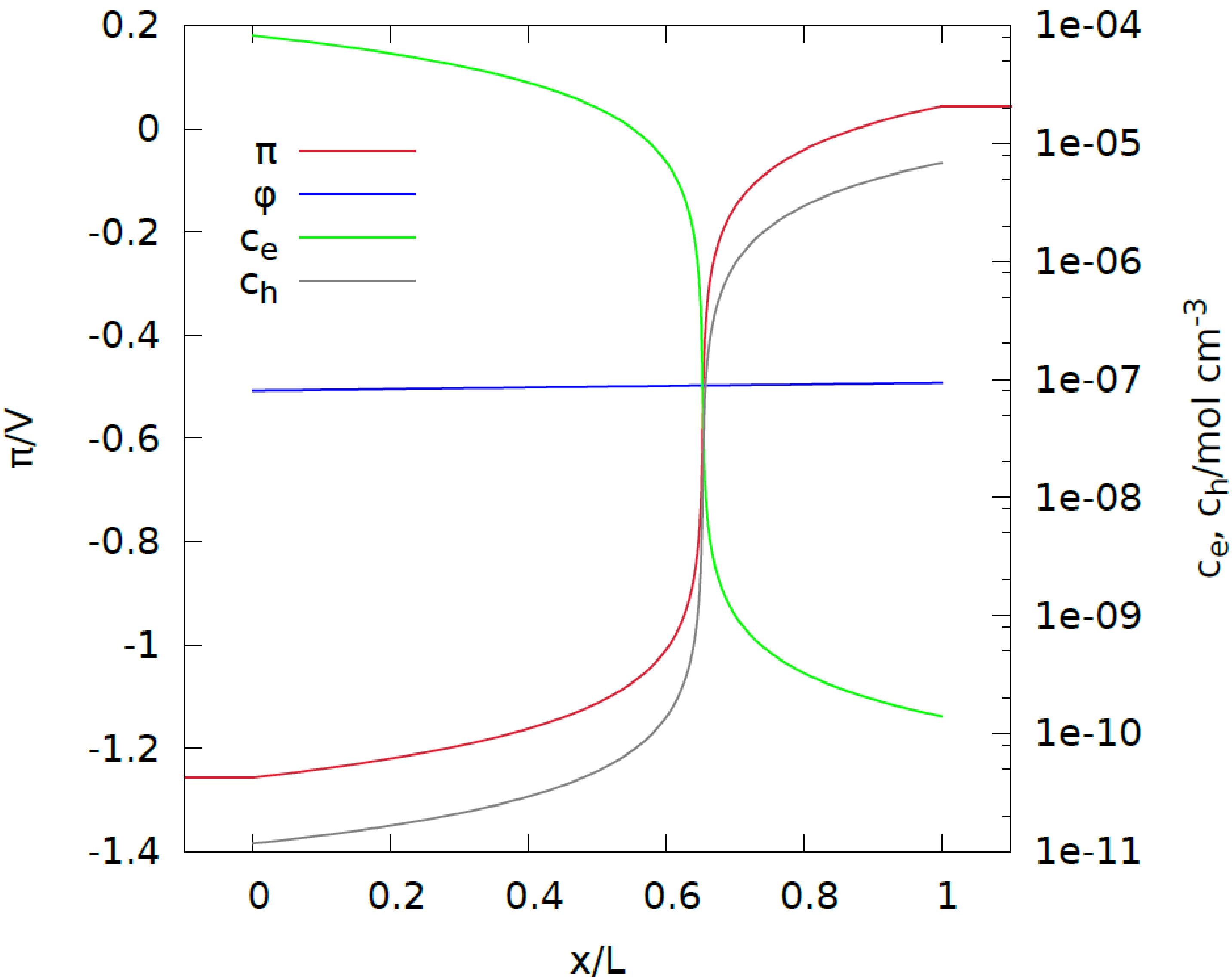
ΔS values from: Ahlgren and Poulsen: SSI 70/71 (1994) 528

n-p is again a different matter only important for EC mode

Data for calculations of electron conduction through the YSZ and p-n recombination heat

Electrolyte thickness/μm	10		
T/K	1123.15	= 850 °C	
pO_2(left electrode)/bar	5.11E-18		
pO_2(right electrode)/bar	1		
Electrode resistance at left electrode/ohm cm^2	0.4		
Electrode resistance at right electrode/ohm cm^2	0.05		
Electronic charge transfer resistance (both electrodes)/ohm cm^2	0.01		
σ_{YSZ}/ S cm^{-1}	0.046		
D_h/ $cm^2 s^{-1}$	1.59E-06		
D_e/$cm^2 s^{-1}$	2.44E-07		
Cell voltage/V	1.3	1.5	1.7
$(\varphi_{right} - \varphi_{left})$/V	0.015	0.024	0.032
Leak current i_{pn}/A cm^{-2}	-0.003	-0.014	-0.077
Total current, i/A cm^{-2}	-0.71	-1.14	-1.57

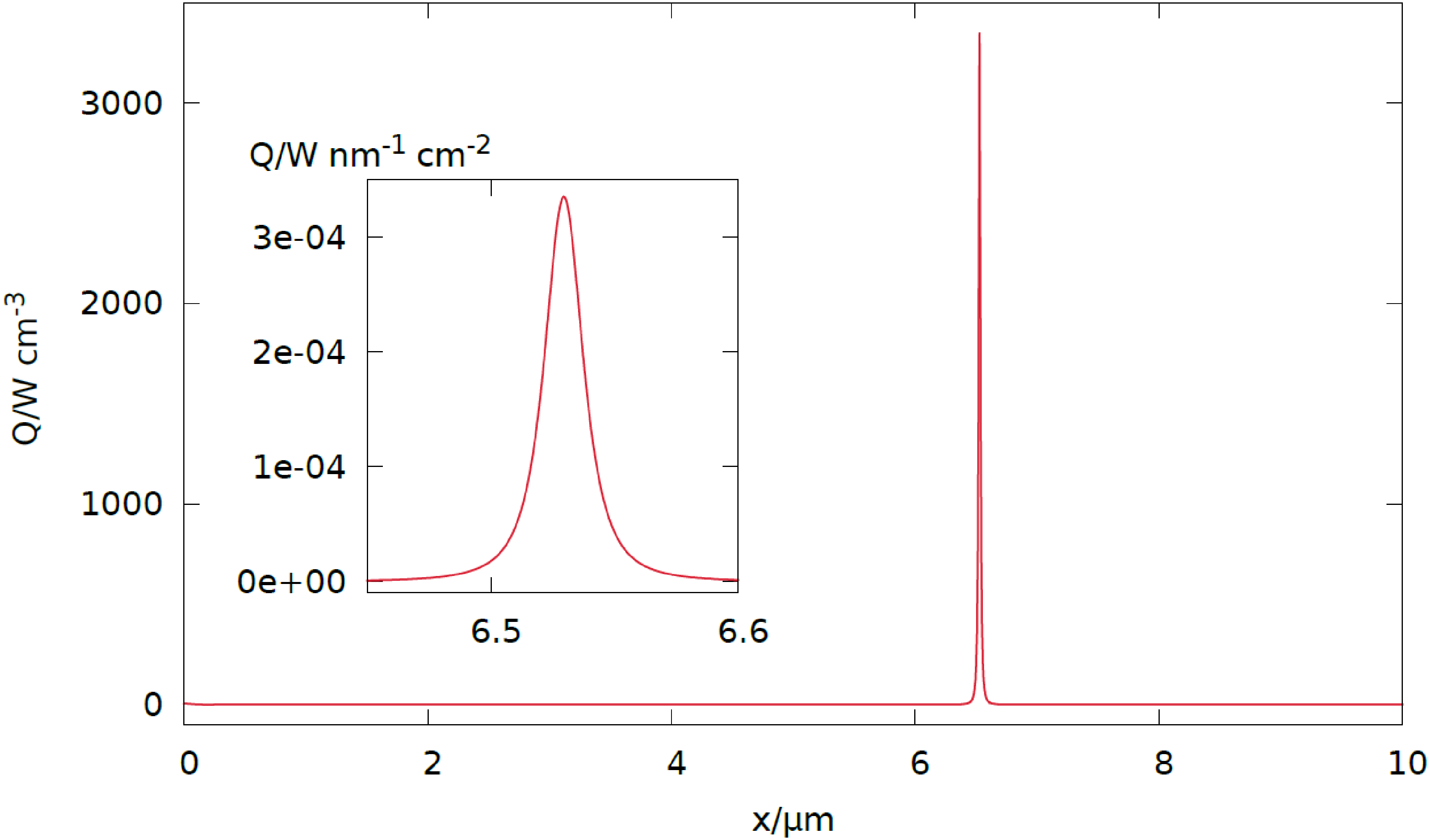
Potentials, e & p concentrations, 1.3 V



T. Jacobsen et al.
to be published

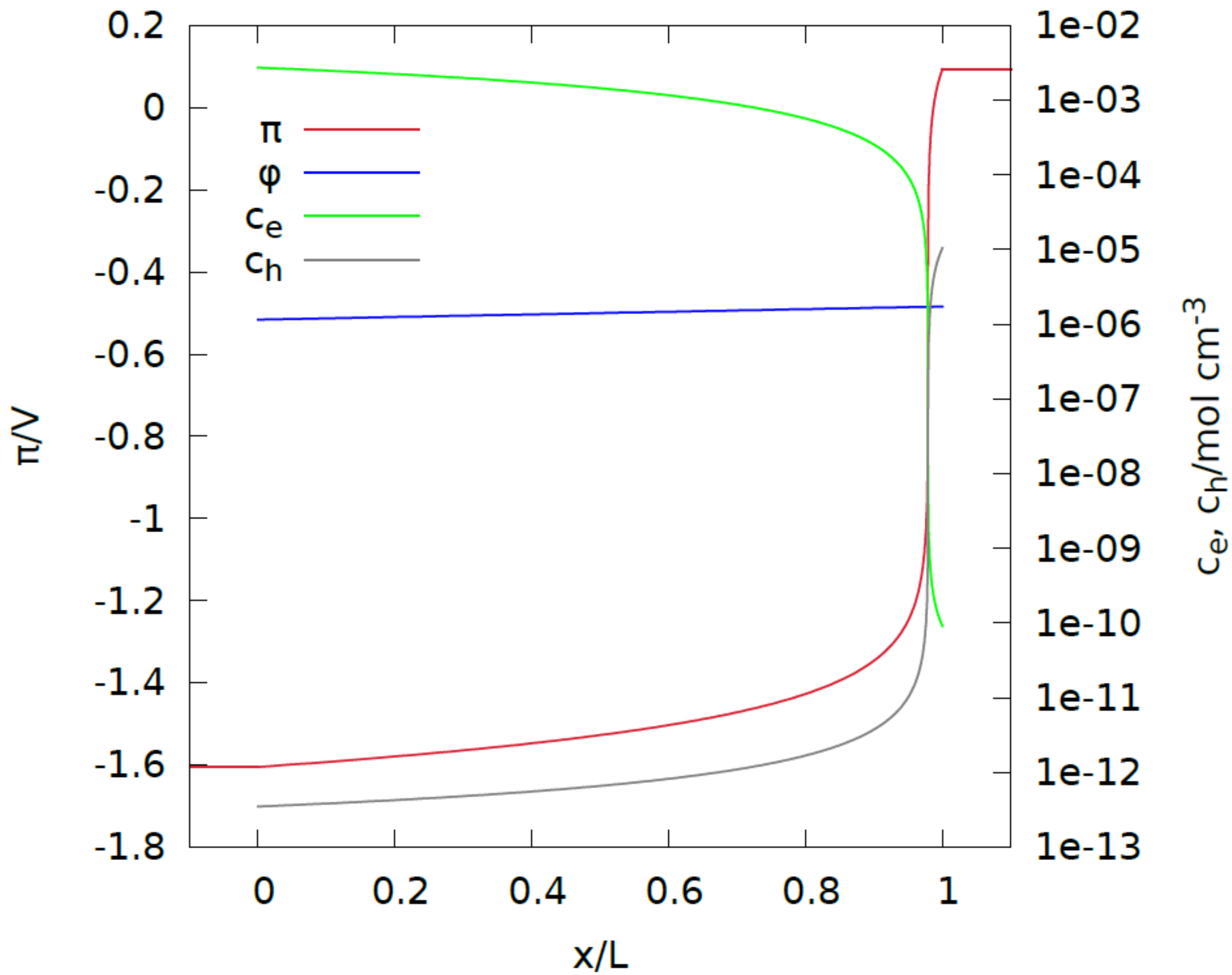
Procedure given in:
T. Jacobsen et al., *ECS Transactions*, **13**, 259 (2008)

Heat evolution at p-n junction - 1.3 V

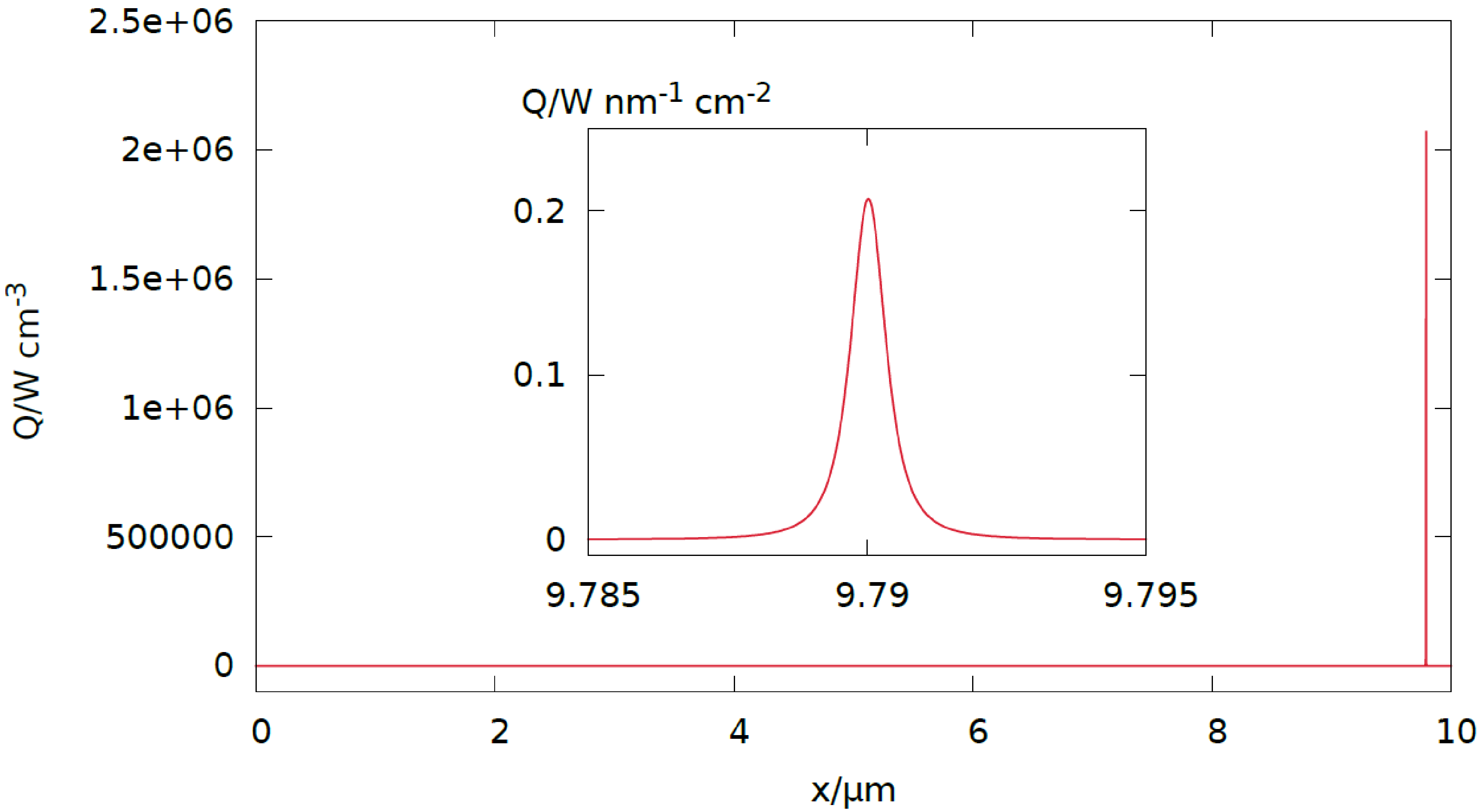


-0.71 A cm^{-2}, e- leak: -3 mA cm^{-2} 850 °C

Potential and e & p concentrations, 1.7 V



Heat evolution at p-n junction - 1.7 V



-1.57 A cm^{-2}, e- leak: -77 mA cm^{-2} 850 °C

Possibilities that we see

1. Our state-of-the-art cell can now run stable over 1000 h at 800 °C with 1 A cm^{-2}

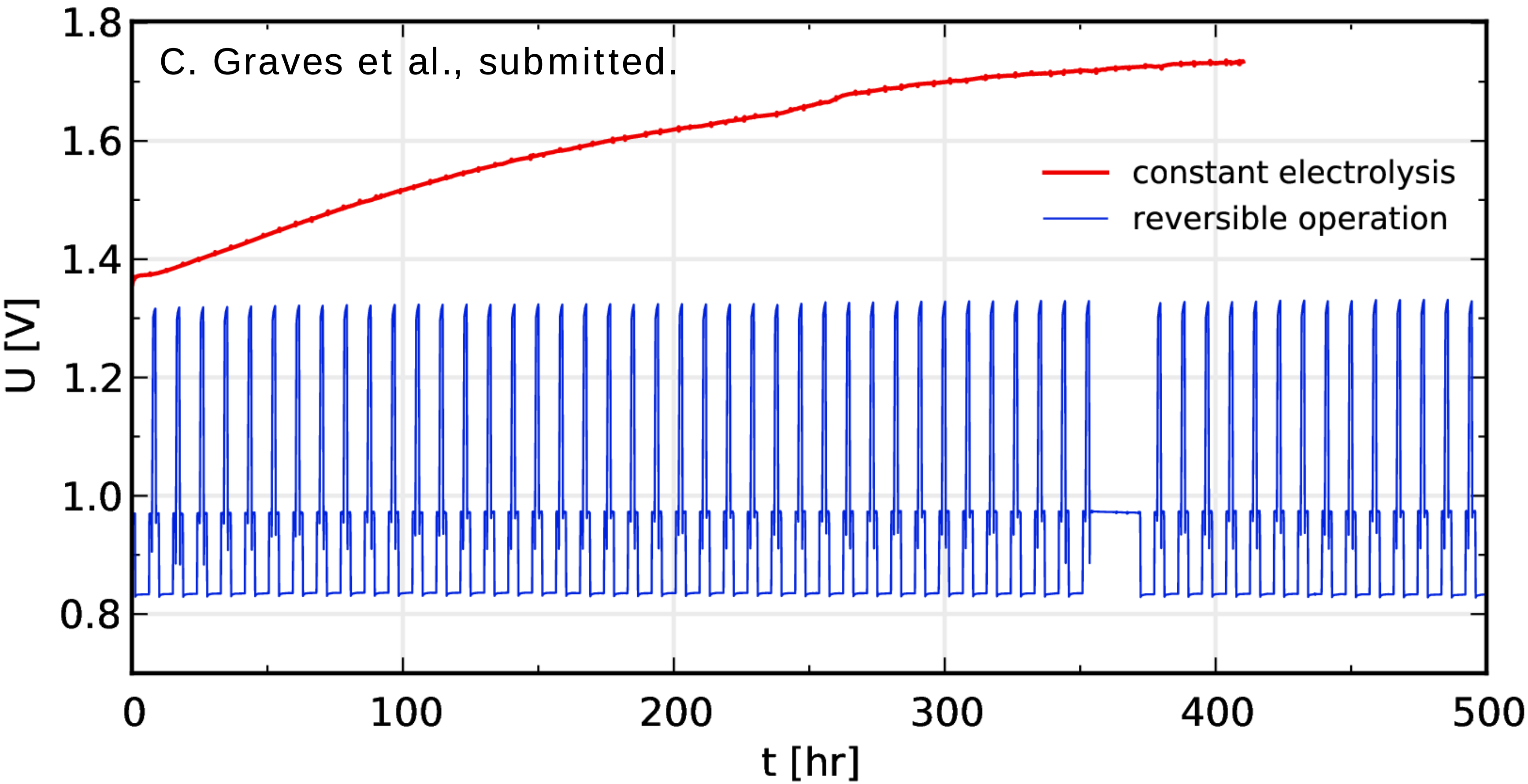
2. We are in the process of improving the basis for safe operation though further detailed measurements and modeling

3. Our improved understanding makes it possible accelerate the R&D further

4. We will look into several aspects of mechanical properties and cell design

5. We anticipate significant improvements though further basic materials and electrochemical research

Reversible operation



SOC stability during constant current electrolysis test compared to reversible cycling test of 1 h EC + 5 h FC. During open-circuit and FC mode, ~25 L/h of $pH_2/pH_2O \approx 50/50$ and EC mode ~13 L/h of $pH_2/pH_2O \approx 10/90$ gas was supplied. Pure O_2 at the O_2-electrode.

Conclusion

In spite of all the limitation we still think:

1. **The reversible SOC has the greatest potential as an energy converter for chemical storage of renewable energy**

2. **The are still many possibilities for further significant improvement of the SOC**

3. **We must put more emphasis on mechanical properties and materials compatibility**

4. **We have already started ☺**

Acknowledgement

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- **Danish Energy Authority** Danish Energy Authority
- **Energinet.dk** ENERGINET.DK
- **EU**
- **Topsoe Fuel Cell A/S** TOPSOE FUEL CELL clean, efficient and reliable
- **Danish Programme Committee for Energy and Environment**
- **Danish Programme Committee for Nano Science and Technology, Biotechnology and IT**
- **The work of many colleagues over the years**

Thank you for your attention!